but were isopropyl substituted benzenes. The following equations are, therefore, proposed in place of equation (II) above

$$CH_3CH_2CH_2—O—SO_3H \longrightarrow (C_3H_6) + H_2SO_4 \qquad III$$

$$(C_3H_6) + C_6H_6 \xrightarrow{H_2SO_4} (CH_3)_2CH—C_6H_5 \qquad IV$$

The (C_3H_6) in the above equation represents the intermediate olefin stage, the olefin being in an "activated" state which readily reacted with benzene. The sulfuric acid probably also activated the benzene nucleus slightly but the activated olefin stage, in this case, was of greater importance.

Experimental Part

Propylene–Benzene Condensation.—Two moles of benzene and various quantities (see Fig. 1) of concentrated sulfuric acid were carefully weighed in a 2-liter three-necked round-bottomed flask (see diagram of apparatus, Fig. 2). The flask was immersed in an ice-bath and maintained at a temperature of 3 ± 1° while propylene was added through a flowmeter at a rate of 21.9 g. of propylene per hour and stirred at a rate of 1100 revolutions per minute.

After propylene had been added for three hours, the flask was removed and the lower layer of sulfuric acid separated. In nearly all cases the weight of the sulfuric acid layer checked closely with the original quantity of acid added. The upper layer was refluxed for three hours with an equal volume of a 20% solution of sodium hydroxide, separated, dried and fractionated. The fractions collected and the physical properties of the four isopropylbenzenes were the same as those previously reported.[1d] For the yields of products see Fig. 1.

The diisopropylbenzene was converted to terephthalic acid and then to its dimethyl ester[1d] to prove its structure.

Ethylene was condensed with benzene under the same conditions that were employed when propylene was used except that the temperature was between 10–20°. By using 82 g. of sulfuric acid with 11 g. of boron fluoride as a promoter, 10.2 g. of ethylbenzene and 1.5 g. of diethylbenzene were formed.

Summary

The influence of the amount of sulfuric acid, the temperature, the time and boron fluoride on the condensation of propylene with benzene has been studied.

Ethylene was condensed with benzene at low temperatures and atmospheric pressure.

A mechanism for the reaction has been proposed.

NOTRE DAME, INDIANA RECEIVED JANUARY 27, 1936

[CONTRIBUTION FROM THE DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Occurrence of Quebrachite in the Stems of Haplophyton Cimicidum

BY E. P. CLARK

In an attempt to isolate the insecticidal material reputed to be present in the stems of *Haplophyton cimicidum*,[1] a crystalline material was obtained which proved to be quebrachite (1-methyl inosite).

Since direct comparison of this substance with an authentic sample of quebrachite was impossible, identification was established by comparing the properties of the isolated material and certain of its derivatives with values already recorded in the literature. The results of this procedure and the method employed to obtain the substance are presented here.

Experimental

Preparation of Quebrachite.—Fifteen hundred grams of ground stems of *Haplophyton cimicidum* was moistened with 750 cc. of water and allowed to stand in a tight container overnight. The drug was then packed in a percolator and exhausted for approximately two hours with sufficient water to yield 8 liters of extract. This liquid was defecated with basic lead acetate, the excess lead removed with sulfuric acid, and the resulting filtrate concentrated, under reduced pressure, to 300 cc. This was diluted to 2 liters with 95% ethanol. The liquid was filtered and concentrated, under reduced pressure, to a very thick sirup. This was heated and diluted to 200 cc. with ethanol. After some time crystallization commenced and was completed within a week or ten days. The crystals were removed, the mother liquor was diluted with an equal volume of hot methanol, and 1 liter of hot acetone was added. The resulting mixture was shaken rapidly to separate the suspended sirupy material, and the relatively clear solution was concentrated under reduced pressure to a thick sirup. This was dissolved from the flask with 50 cc. of ethanol, and the liquid allowed to crystallize. The total yield of crude quebrachite was usually 10 to 11 g.

The crude material was purified by dissolving 1 g. in 2 cc. of hot water, filtering through Norit, and adding 8 cc. of hot ethanol to the filtrate. Crystallization began at once and was soon completed. By working over the mother liquors, recovery was practically complete.

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(1) This material was obtained through the coöperation of the Mexico City Laboratory of the Division of Fruit Fly Investigations, Bureau of Entomology and Plant Quarantine.

Properties of Quebrachite.—Purified quebrachite consists of colorless rhombs and six-sided and wedge-shaped forms which melt at 192–193° (corr.). Under reduced pressure the material readily sublimes, and in 5% aqueous solution it has a specific rotation of $[\alpha]^{20}\text{D}$ −81.2°. Tanret[2] reported the melting point as 186–187° and αD as −80°.

Calcd. for $C_7H_{14}O_6$: C, 43.28; H, 7.27; OCH_3 (1), 15.98. Found: C, 43.26; H, 7.25; OCH_3, 15.94.

The optical crystallographic characteristics of the material were determined by George L. Keenan, of the Food and Drug Administration.

The rhomb-like and wedge-shaped forms predominate. In parallel polarized light (crossed nicols) the plates show low-order colors and extinguish in a hazy manner. In convergent polarized light (crossed nicols) most plates are sections perpendicular to the acute bisectrix, although the biaxial interference figures are only faintly shown. The refractive indices of the material, determined by the immersion method, are: η_α, 1.546; η_β, 1.552; η_γ, 1.572; all ±0.003.

The β- and γ-indices were found most frequently.

***l*-Inosite from the Hydrolysis of Quebrachite.**—One gram of quebrachite dissolved in 5 cc. of hydriodic acid, sp. gr. 1.7, was heated in a boiling water-bath for one and one-half hours. Eight volumes of boiling alcohol were added, and the mixture was placed in an ice-bath. Crystallization began at once and was soon completed. The yield was practically quantitative.

The inosite recrystallized by adding boiling alcohol to a hot, concentrated, clarified aqueous solution consisted of heavy, colorless, irregular plates which began to sinter at 195° and melted and flowed at 242–243°. In 5% aqueous solution its specific rotation was $[\alpha]^{20}\text{D}$ −64.7°. Tanret[2] reported the melting point as 238° and the specific rotation of the hydrate, $C_6H_{12}O_6\cdot 2H_2O$, as $[\alpha]\text{D}$ −55°. This calculated to the anhydrous form is −66°. Its optical crystallographic properties were as follows. In parallel polarized light (crossed nicols) first and second order polarization colors are usually shown. In convergent polarized light (crossed nicols) plates frequently occur showing biaxial interference figures characteristic of sections perpendicular to the acute bisectrix. The substance is optically negative, and therefore η_β and η_γ lie in the two positions at right angles to each other in the plane of the plates, and the η_α direction lies perpendicular to the plates and can only be measured by turning the plates on edge. The axial angle is not large. The refractive indices as determined by the immersion method are η_α, 1.553 (only approximate since it is difficult to orient the material to show this index); η_β, 1.562; η_γ, 1.566 (±0.003).

The birefringence is moderate.

l-Inosite hexabenzoate, prepared by the Schotten–Baumann method and recrystallized from *n*-butyl alcohol, melted at 247°. Tanret[2] gives 252°.

Summary

Quebrachite was found in the stems of *Haplophyton cimicidum* to the extent of approximately 0.7%. A method for its preparation is given, and new and revised physical data are presented for quebrachite and *l*-inosite.

WASHINGTON, D. C. RECEIVED APRIL 24, 1936

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[2] Tanret, *Compt. rend.*, **109**, 908 (1889).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

1-Chloro-2-methyl-2-propanol from 1,2-Dichloro-2-methylpropane[1]

BY C. E. SPARKS AND R. E. NELSON

Introduction

Pogorshelski[2] reports that 2-methyl-1,2-propanediol is obtained on treating 1,2-dichloro-2-methylpropane with hot potassium carbonate solution.

The purpose of this investigation is to determine whether 1-chloro-2-methyl-2-propanol is formed in the liquid-phase hydrolysis of 1,2-dichloro-2-methylpropane. The 1,2-dichloro-2-methylpropane was prepared, unless otherwise specified, by converting 2-methyl-2-propanol into 2-chloro-2-methylpropane and chlorinating the latter.

Discussion

1-Chloro-2-methyl-2-propanol was the chief product isolated from the liquid-phase hydrolysis of 1,2-dichloro-2-methylpropane under neutral, slightly basic or slightly acidic conditions. That 1-chloro-2-methyl-2-propanol is formed is established by the boiling point of the product, the fact that it forms 1,2-dichloro-2-methylpropane when treated with concentrated hydrochloric acid and its conversion into 1,2-epoxy-2-methylpropane.

Table I shows, in general, decreased yields of 1-chloro-2-methyl-2-propanol when basic components were added to the hydrolysis mixtures.

Experimental

All of the hydrolysis experiments were performed in the same apparatus which consisted of a five-liter, three-necked

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(1) Based upon a portion of a thesis submitted by C. E. Sparks to the Faculty of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1936.

(2) Pogorshelski, *Chem. Zentr.*, **76**, I. 667 (1905).